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# THE OXIDATION OF FERROUS SULPHATE TO FERRIC SULPHATE BY MEANS OF AIR

By


JAMES STEWART MACHIN

A. B. Westminster College, 1921

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
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IN THE GRADUATE SCHOOL OF THE UNIVERSITY  
OF ILLINOIS, 1922

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THE GRADUATE SCHOOL

JULY 28, 1922

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY JAMES STEWART MACHIN  
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FERRIC SULPHATE BY MEANS OF AIR  
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THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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In Charge of Thesis

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Recommendation concurred in\*

Committee

on

Final Examination\*

100-125

\*Required for doctor's degree but not for master's



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# THE OXIDATION OF FERROUS SULPHATE TO FERRIC SULPHATE BY MEANS OF AIR

## INTRODUCTION

Among the wet methods for the extraction of copper from its ores, leaching with ferric sulphate solution is among the oldest if not the oldest process.

The leaching of copper ores by this method has been practiced at Rio Tinto, Spain, since 1839 and today the process is still being applied there with greater success than at any other place. The process there is called cementation and the product cement copper.

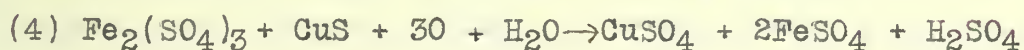
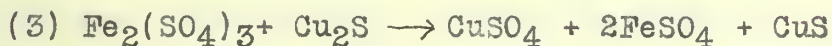
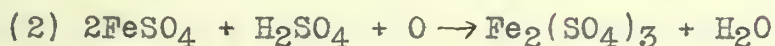
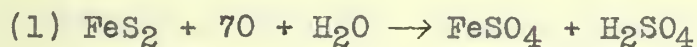
Formerly, the ores there were treated by ordinary smelting methods, but the sulphur dioxide liberated destroyed the vegetation in the surrounding country and became such a nuisance that further treatment of the ores by the then used process was prohibited by law.

The application of the modern method was the result of investigations conducted by FELIPE PRIETO of Seville. To him was issued a royal patent, published in the "Official Gazette" September 9, 1845 described as "An original invention for a chemical discovery for utilizing the copper bearing pyritic minerals no matter how low the percentage may be".(1)

The method consists in wetting the ore heaps with water, and with proper control of ventilation of the pile, the mineral is oxidized by air and moisture, and the  $\text{CuSO}_4$  which is formed is washed out.



The ore is principally  $\text{Cu}_2\text{S}$  and  $\text{FeS}_2$ . Advantage is taken of the following reactions, suggested by Charles H. Jones. (2) (3)



It is seen from these equations that the  $\text{Fe}_2(\text{SO}_4)_3$  is the compound which reduces the copper sulfides to a soluble form. Any copper present as the oxide or carbonate would also undoubtedly be dissolved by the sulphuric acid formed in the reactions with the sulfides.

The success of this process at Rio Tinto naturally led to other attempts to leach ores with ferric sulphate solutions. Ores whose copper content was so low that it would not pay to treat them by ordinary smelting methods seemed especially suited to this treatment.

Ferric sulphate, however, is a comparatively expensive reagent where the conditions for its production are not so favorable as at Rio Tinto. Moreover, it is reduced to ferrous sulphate in the process. It therefore became necessary to find some cheap means for converting this ferrous sulphate back to ferric sulphate or the expense of the process would become prohibitive.

This feature is unimportant at Rio Tinto because the ferric sulphate used is formed in the ore heap as is shown by the equations given above. The liquors are simply allowed to run to waste in some cases after the copper has been removed by precipitation on scrap iron.





It would seem that a part of the copper might be lost thru incomplete removal by the scrap iron. This loss, if there is one, could be largely eliminated by returning the waste liquors to the ore heaps were it not for the fact that the basic salts of iron, which are precipitated when solutions of ferrous sulphate are exposed to the air, have a tendency to clog the ore by forming a film which breaks up the capillarity of the ore, preventing access of the solvent to the interior of the piece. Thomas (4) found also that the presence of much ferrous sulphate hindered the solvent action of ferric sulphate on  $\text{Cu}_2\text{S}$ .

For the reasons just discussed, it became imperative to find some cheap, fairly efficient and fairly rapid way to oxidize the ferrous sulphate liquors to ferric sulphate. If this could not be done, the ferric sulphate leaching process was inapplicable in places where the character of the ore and other conditions are less favorable than at Rio Tinto.

It was in the hope that some light might be thrown on this problem of the regeneration of the ferric-sulphate liquors, that this investigation was undertaken.





## REVIEW OF THE LITERATURE

A good many articles have been written on the ferric sulphate method, and several processes for the wet extraction of copper have been patented, which are based on the regeneration of the ferric sulphate leach liquors.

Perhaps the most interesting and instructive article is W. L. Austin's (5) (6) account of experiments carried out at Cananea Mexico, by the Cananea Consolidated Copper Company.

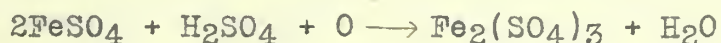
He describes the process by which the oxidation of the ferrous sulphate solutions was carried out.

A large tank which gave a working head of eleven feet, eight inches, was used to contain the solution. The belief was expressed that a working head of eighteen feet would give better results. The solution was heated by means of a steam coil and preheated air was forced in from the bottom agitating the solution violently. In one run which was kept going for thirty two hours, starting with a solution containing  $\text{FeSO}_4$ , 12.1%, and  $\text{Fe}_2(\text{SO}_4)_3$ , 1.6%, there was present at the end,  $\text{FeSO}_4$ , 5.1% and  $\text{Fe}_2(\text{SO}_4)_3$ , 7.0%. About 57.85% of the original  $\text{FeSO}_4$  has been converted. Trouble was experienced from a basic sulphate which formed in the tank.

In regard to this basic sulphate, Austin says, "The reactions which take place when an attempt is made to oxidize  $\text{FeSO}_4$  to the ferric condition without the presence of free acid are very complicated. Basic ferric salts, of which there are many varieties, invariably form and are precipitated, thereby causing the loss of a large part of the iron unless free  $\text{H}_2\text{SO}_4$  has been added in amounts

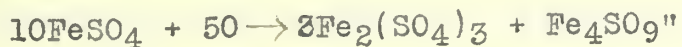


necessary to produce the neutral  $\text{Fe}_2(\text{SO}_4)_3$ . For the purpose specified (the formation of neutral ferric sulphate), ten parts of ferrous sulphate require two parts of concentrated sulphuric acid. The reactions which occur are indicated in the following equation:



"If a solution of ferric sulphate is heated with ferric hydrate there results a deep brown liquor containing a more basic salt - two thirds as much sulphuric acid combined with the same amount of iron as in the neutral salt. This basic salt is also formed when a solution of ferrous sulphate is slowly oxidized by contact with the air, while at the same time a still more basic salt is produced (with one sixth as much sulphuric acid as in the neutral sulphate) together with other soluble sulphates and the neutral ferric sulphate.

"The basic salt, containing two thirds as much sulphuric acid as the neutral sulphate, is decomposed by heating or by dilution of the solution, the resulting products being neutral ferric sulphate and a yellow precipitate containing the one sixth salt referred to above. These two last named ferric compounds predominate when a solution of ferrous sulphate is oxidized by exposure to the air, and are claimed by some authorities to be the final products from the oxidation described.



If this equation be representative of the reaction, it is evident that 40% of the iron and 10% of the acid is lost if the solution is oxidized without the presence of free acid.

The reaction was found to be very slow and the problem of





oxidizing the ferrous sulphate solution, it was thought, was the most important detail of the successful application of the process.

The Irving Leaching Process:<sup>(7,8,9)</sup> - In this process, the  $\text{FeSO}_4$  solution is oxidized by a steam jet which agitates it violently, bringing it in contact with the air and supplying heat. The basic sulphate formed is dissolved by adding  $\text{H}_2\text{SO}_4$ .

In an article entitled "Some Experiments in Heap Leaching Copper Ores", (10), Geo. D. Van Arsdale says, "No practicable method of cheaply converting for leaching purposes ferrous to ferric iron has been worked out, and it seemed evident that the only sufficiently cheap method was the partial conversion to be obtained by evaporation. Further, if this evaporation were carried on in intimate contact with the ore being leached, probably a better and quicker extraction could be obtained. Accordingly, the following steps were adopted as a method for preliminary tests: (1) Wetting the ore with excess of solution containing ferrous sulphate and a small amount of ferric sulphate; (2) Allowing the ore to drain and air dry thoroly; (3) Precipitating the copper from the resulting liquor by iron, returning the liquor to ore and repeating.

It will be noted that this method is identical with that practiced at Rio Tinto, except that the ferrous sulphate is supplied whereas at Rio Tinto this is unnecessary because of the nature of the ore, the iron salts being formed in the heap.

Van Arsdale found that, using the method outlined above, in which a neutral solution of ferrous sulphate was used, after eight or ten leaching cycles the solution of copper practically ceased. The probable reason was that a yellowish precipitate of ferric hydroxide



or basic sulphate formed and broke up the capillarity of the ore, thus preventing the solvent action of the solutions.

In a second series of experiments, a small amount of acid was added to the lixivant to prevent the formation of this precipitate. This gave better results and the recovery of copper reached a fixed rate of about 2% of the copper present, for each leaching cycle, instead of decreasing to zero as when the neutral ferrous sulphate was used.





### III. THEORETICAL

All previous experiments on the oxidation of ferrous sulphate solutions with air seem to show that the reaction represented by the equation  $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$  is a very slow one even under favorable conditions, and that the energy consumed (when supplied in the form of heat) in attempting to hasten it is very great.

If we calculate the heat of the reaction according to Hess's Law, from the heats of formation\* of the compounds involved in the reaction as represented by the equation in the preceding paragraph, it will be seen that heat evolved by the reaction is equivalent to 176,400 calories per gram mole of  $\text{Fe}_2(\text{SO}_4)_3$  formed. This heat will of course be dissipated to the surroundings. Then according to LeChatelier's principle, the reaction once started should proceed with increasing velocity toward the right. That the reaction does start and does proceed, though slowly, toward the right is well known. Why does it not proceed rapidly and spontaneously to completion? There is no tendency to come to equilibrium because a solution of  $\text{Fe}_2(\text{SO}_4)_3$  has no tendency to reduce except in the presence of strong reducing agents such as nascent hydrogen and hydrogen sulphide, and even then, care must be used if complete reduction is desired. On the other hand,  $\text{FeSO}_4$  and all other ferrous compounds show a tendency to pass over to the ferric state. They are converted quickly and completely in the presence of strong

\*Heats of formation taken from Landolt-Bornstein's TABELLEN.



oxidizing agents. Their oxidation is also easily and quickly accomplished by electrolytic methods.

All of these facts would indicate that the oxidation of  $\text{FeSO}_4$  to  $\text{Fe}_2(\text{SO}_4)_3$  in the presence of air and free acid should proceed spontaneously and rapidly to completion. As a matter of fact, it does not. We have a reaction for which all the driving forces are favorable and yet it does not go. This being the conclusion, the problem seems to be one of, first finding a suitable catalyst, and second, making the mechanical conditions for the oxidation as favorable as possible.



#### IV. EXPERIMENTAL

As preliminary experiments, solutions of ferrous sulphate were aerated by bubbling air through them. The factors varied were: concentration of ferrous sulphate, concentration of free sulphuric acid, and temperature. The temperatures used were room temperature, 55°, 80° and 95°C.

These tests showed that the concentration of ferrous sulphate within the limits used in the experiments (2% to 7% by weight) makes little difference in the velocity of the reaction; that the reaction goes somewhat better in a neutral solution than in an acid solution; that temperature has a marked effect on the velocity of the reaction, increase of temperature accelerating it greatly. The period of these experiments was twenty-four hours, divided into two periods of twelve hours each. The results varied from 2.5% oxidation in the acid solutions which were aerated at room temperature, to 30.9% oxidation in the neutral solutions which were aerated at 95°C.

In the neutral solutions, basic salts of iron were precipitated. These salts seemed to be the same whether formed at the higher or the lower temperatures. Samples were analyzed quantitatively for iron and sulphur, the method of analysis being as follows:

The precipitates were filtered onto weighed Gooch filters and dried for two hours at 110°. The residues were then dissolved with hot concentrated hydrochloric acid. The iron was precipitated as ferric hydroxide and determined as  $\text{Fe}_2\text{O}_3$  by the ordinary gravimetric method. The filtrate from the ferric hydroxide was made





acid and the sulphur precipitated and determined as barium sulphate.

The results show the composition of the samples to have been Fe 68.95%,  $\text{SO}_4$  9.71%. This leaves 21.34% to be accounted for as oxygen or as oxygen and hydrogen. These figures represent an average of four determinations which were consistent within 0.4 of one per cent. This composition would indicate a mixture of compounds, part of which are probably hydroxides, since no simple formula would fit this composition unless it have a very large number of iron and oxygen atoms and a small number of  $\text{SO}_4$  groups. Presumably, then, it may be considered a mixture of basic ferric sulphate and colloidal ferric hydroxide.

On ignition, these salts decompose, leaving as a residue a mixture of the oxides of iron, some of which are magnetic.

Since the basic salts do not form in acid solution and it is obvious that  $\text{H}_2\text{SO}_4$  in some form must be supplied if the normal  $\text{Fe}_2(\text{SO}_4)_3$  is to be formed from  $\text{FeSO}_4$ , it was decided to try to use  $\text{SO}_2$  as a basis for the acid at the same time the solution was being oxidized.

A mixture of  $\text{SO}_2$  and a large excess of air was passed thru a tube furnace filled with crushed pumice which had been impregnated with  $\text{Fe}_2\text{O}_3$ . The  $\text{Fe}_2\text{O}_3$  was expected to catalyze the union of a part of the oxygen of the air with the  $\text{SO}_2$  to form  $\text{SO}_3$ . The pumice was used to prevent the  $\text{Fe}_2\text{O}_3$  from packing and to present a large surface of the catalyst to the gas mixture. The furnace was heated to  $650^\circ \text{C}$ . as that is about the temperature given by Partington(11) as the most favorable for the catalytic action of  $\text{Fe}_2\text{O}_3$ . on the union of  $\text{SO}_2$  and oxygen. The hot gases from the furnace were discharged directly into a solution of ferrous sulphate which was





stirred vigorously with a motor.

In using this apparatus, it was found that unless the ratio of air to  $\text{SO}_2$  was kept very large, a part of the  $\text{SO}_2$  came through into the solution and, since it is a reducing agent, almost entirely prevented the oxidation of  $\text{FeSO}_4$  to  $\text{Fe}_2(\text{SO}_4)_3$ . When, however, a very small amount of  $\text{SO}_2$  was mixed with a relatively large amount of air, the oxidation went forward slowly.

In one 10-hour run which may be taken as representative, the solution, containing at the start of the run 5% by weight of  $\text{FeSO}_4$  and only a trace of  $\text{Fe}_2(\text{SO}_4)_3$ , was subjected to the action of the hot gases as they were discharged from the furnace. Water was added from time to time to make up for losses by evaporation. A thermometer in the solution showed an average temperature of  $70^\circ$ . Samples were taken at intervals of two hours and analyzed for iron present as  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ . No basic salts were precipitated.

The potassium permanganate method was used in these and all other analyses made for ferrous and ferric iron in connection with these experiments. Ten cc. of the iron sulphate solution were titrated against potassium permanganate solution, giving the iron present as  $\text{Fe}^{++}$ . A second ten cc. of the iron sulphate solution were run through a Jones reductor and then titrated against the permanganate, giving the total iron present. The difference of course gives that part of the iron present in the ferric state.

The results, which were very disappointing were as follows:



<u>TIME</u>	<u>% FE<sup>++</sup></u>	<u>% FE<sup>+++</sup></u>
0 hrs.	99.5	0.5
2 "	97.2	2.8
4 "	94.8	5.2
6 "	93.9	6.1
8 "	93.7	6.3
10 "	93.4	6.6

There was appreciable oxidation during the first six hours, but after that, the reaction though continuous was very slow. The results on the whole were less satisfactory than when air alone was used. The only gain over air was that acid did not have to be added and this was more than offset by the heat used in keeping the temperature of the furnace up to 650°.

It became evident that heat was inefficient as a catalyst and that the SO<sub>2</sub> method here used for supplying the needed sulphuric acid was unsatisfactory.

Various substances were successively tried as catalysts with uniformly poor results.

Animal charcoal was suspended in the solution and the whole stirred vigorously with a motor while air was passed through. This experiment was tried both with and without heating the solution. Precipitated silica and manganese dioxide were tried under the same conditions as the charcoal. There seemed to be no tendency for any of these to catalyze the reaction.

It was next decided to try the effect of the oxides of some of the heavy metals which have two or more oxides as it is known that some of these oxides will catalyze certain reactions. The





metals which meet this requirement include chromium, cobalt, lead, manganese, and mercury among the common metals. Others such as platinum are unsatisfactory on account of the expense if for no other reason. Of the oxides of the more common metals mentioned, it happens that manganese dioxide is the only one that is not soluble in dilute solutions of sulphuric acid.

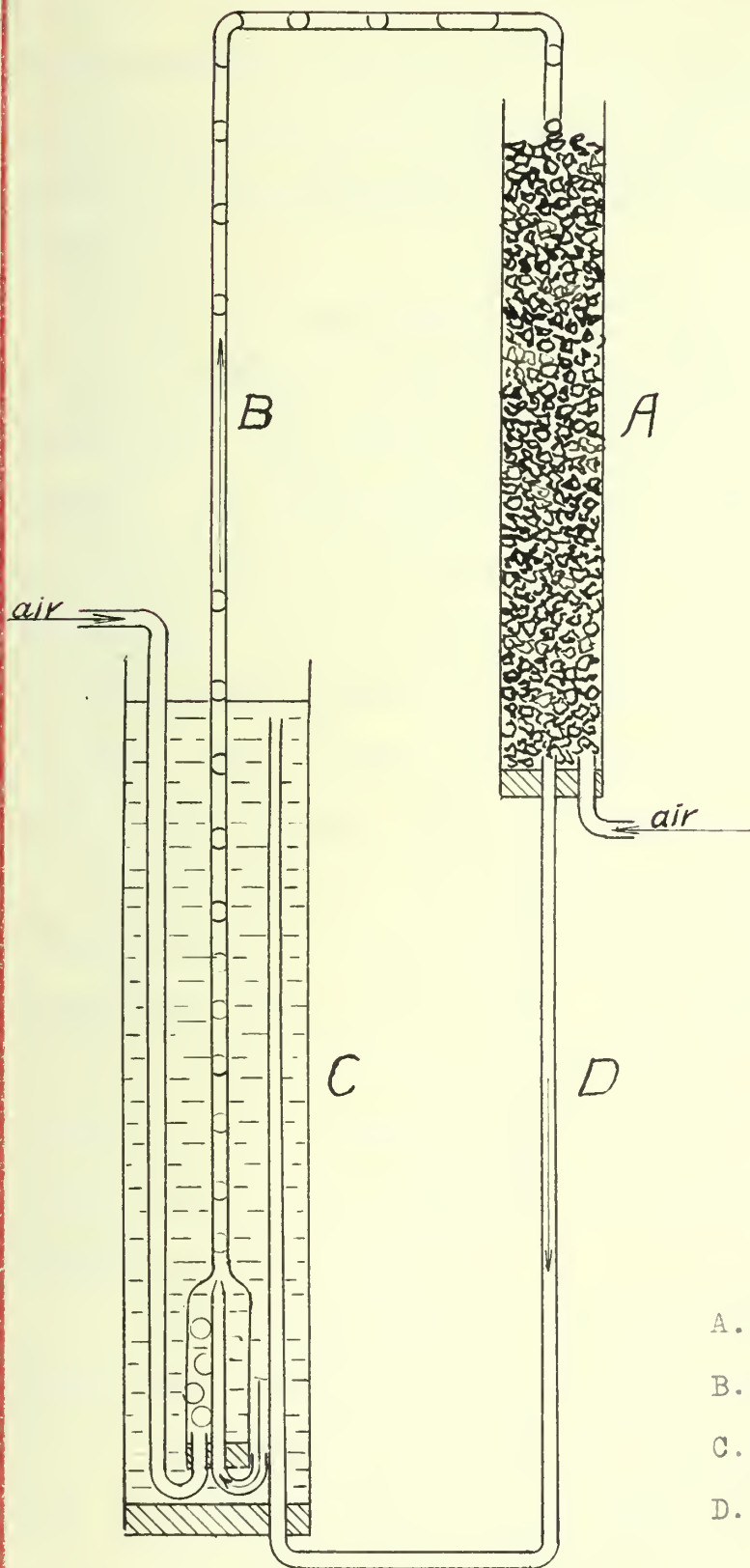
At this point, two pieces of apparatus were devised with the idea of improving the mechanical conditions for the oxidation by providing greater surface contact between the solution and the air and between the solution and the catalyst.

In the first, the solution was made<sup>to</sup> flow over the surface of a large clay crucible (area of surface about 420 square centimeters) at the rate of one hundred cubic centimeters per minute. No heat or catalyst was used and the results were unsatisfactory.

In the second apparatus, a diagram of which appears on the next page, the solution was caused to trickle down through a tower, packed loosely with the catalytic material, while air was blown into the tower from the bottom. The solution, after passing over the catalyst and at the same time being aerated, drained back into the reservoir and was returned to the top of the tower again by a lift pump operated by a current of air. The cycle could be made continuous as long as desired.

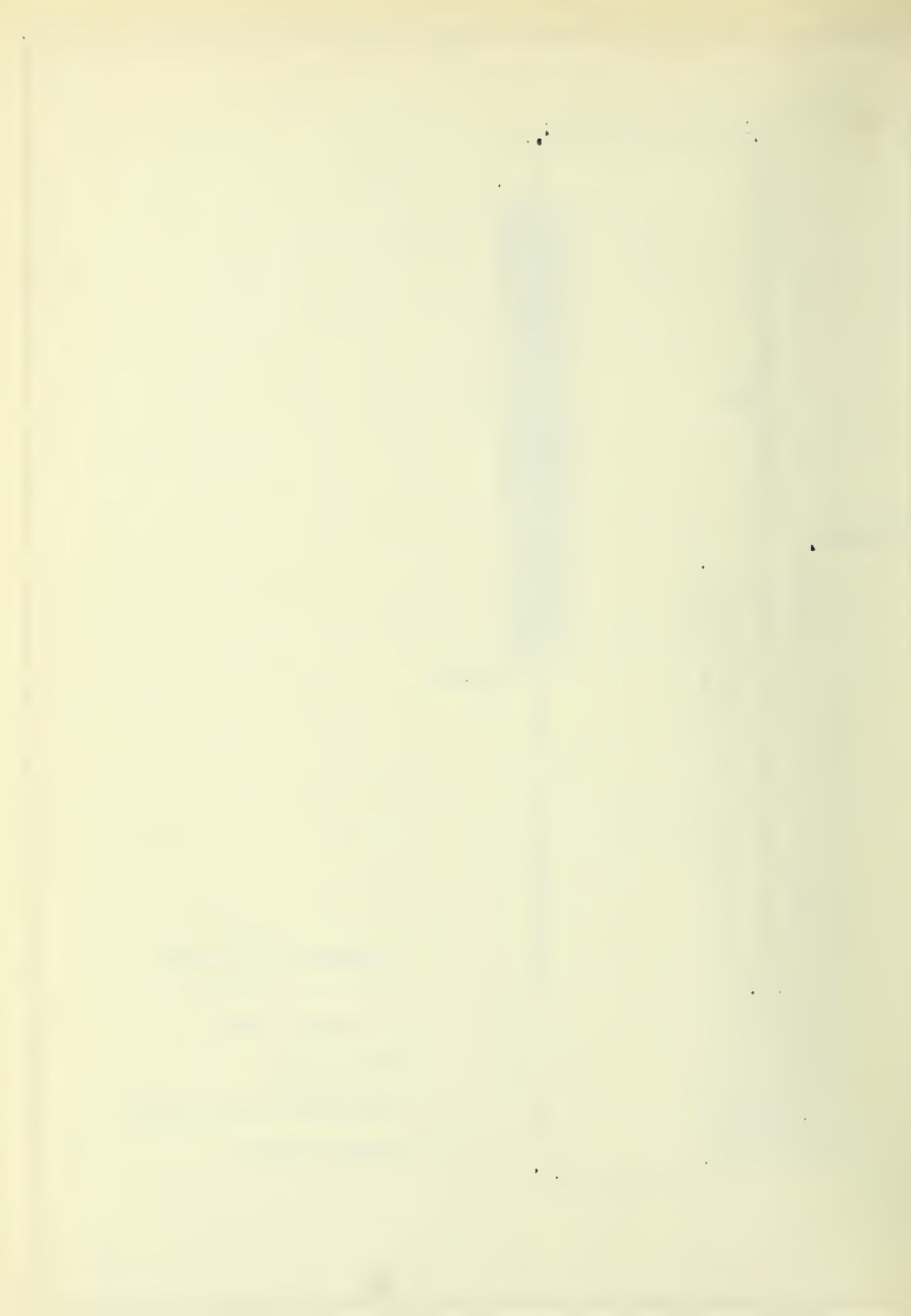
As packing for the tower crushed pumice which had been impregnated with manganese dioxide was used. The impregnation of the pumice was accomplished by boiling with a concentrated solution of  $\text{KMnO}_4$  followed by heating to red heat in a muffle furnace for one hour, or reducing the  $\text{KMnO}_4$  with alcohol and drying.





-OXIDIZING APPARATUS-

- A. Catalyst tower
- B. Lift pump
- C. Reservoir for solution
- D. Return drain





A run was made with this material as packing for the tower. The particles of manganese dioxide washed off easily and became coated with the basic salts described above, but the results were sufficiently encouraging to warrant further investigation along this line.

In the next experiment, the tower was packed with lumps of mineral manganese dioxide (pyrolusite) graded to about one fourth inch sizes. The height of the column of catalyst was eighteen inches. The solution used was one normal with respect to  $\text{FeSO}_4$  and contained the theoretical amount of  $\text{H}_2\text{SO}_4$  necessary to form  $\text{Fe}_2(\text{SO}_4)_3$ . Air was blown into the bottom of the tower as rapidly as was possible without blowing the solution and the catalyst out of the top. The solution was run into the top of the tower at the rate of one hundred cubic centimeters per minute.

After all of the solution had passed through the tower once, (the capacity of the apparatus was approximately two liters) a sample was taken for analysis. The results exceeded all expectations. It was found that eighty-two per cent of the iron had been oxidized to the ferric state. By the time the solution had passed five times over the catalyst, the oxidation was practically one hundred per cent complete.

This result has been repeated, without changing the catalyst, using solutions of varying  $\text{FeSO}_4$  concentration. The catalyst becomes coated with the basic sulphates, especially where the pieces touch each other or the walls of the tower. It is, however, easily cleaned without removing from the tower by washing with a little dilute sulphuric acid. Where solutions are used to which the



theoretical amount of acid has been added for the formation of normal ferric sulphate, it is a long time before the lumps of manganese dioxide become sufficiently coated to interfere seriously with their catalytic efficiency. It is thought that if larger lumps were used, the tendency to become coated would be less because as stated before, the coating formed more noticeably where the pieces were in contact with each other.

The same manganese dioxide was used for all runs and during these experiments showed no tendency to become "poisoned" or lose its efficiency except on account of the coating described in the preceding paragraph.



## V. SUMMARY

A process has been developed for the rapid oxidation of ferrous sulphate in solution to ferric sulphate by means of air. No heat or other form of energy is required except that necessary for circulating the solution and blowing the air into the tower.

The apparatus is simple and capable of modification to suit large scale operations. By increasing the height of the catalyst column or by connecting a number of towers in series, it should be possible to make the process continuous and at the same time to secure practically one hundred per cent oxidation.

The catalyst in view of the amount required is comparatively inexpensive. The manganese ore has been quoted on the market within the year at fifty-five dollars a ton.





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